PHYSICAL REVIEW A VOLUME 5, NUMBER 4 APRIL 1972

Triangular Lattice Gas*

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(Received 27 September 1971)

The planar triangular lattice gas with repulsive nearest-neighbor and attractive second-nearest-neighbor interactions is solved in the Bethe-Peierls approximation. The maximum temperature of transition between disordered and ordered phases occurs at a density of one-third. All transitions are first order with a discontinuity in the order parameter at the transition. Deficiencies in the approximation are noted and discussed.

I. INTRODUCTION

As a model of physical absorption of gases on a substrate providing a triangular array of absorption sites, we study the planar triangular lattice gas. Graphite is a paradigm of a substrate providing such an array of sites. The interaction between absorbed noble gases is approximated by assuming an infinite repulsion between atoms on the same site, a large but finite repulsion on nearest-neighbor sites, a weak attractive interaction between atoms on second-neighbor sites, and no interaction otherwise. The problem is isomorphic to the planar triangular Ising model with finite antiferromagnetic nearest-neighbor coupling, and weak ferromagnetic second-neighbor coupling.

The triangular Ising problem with antiferromagnetic coupling only has been solved exactly[1] in zero external magnetic field, which corresponds to a density of one-half in the lattice gas. The result is that there is no transition to an ordered state at any finite temperature. The lattice gas with infinite nearest-neighbor repulsion has been studied by transfer-matrix methods,[2] by Kikuchi approximation,[3] and by series expansions.[4] This model does show a transition with density to an ordered state, but there is disagreement as to whether the transition is first[2,3] or second order.[4] Lastly, the Ising model with antiferromagnetic coupling only has been studied in the Kikuchi approximation.[5] A maximum transition temperature is found at an average magnetization per site equal to one-third, but it is unclear whether the difference of sublattice magnetization changes discontinuously across the transition (first order) or continuously (second order).

The approximation method we apply to the model with the structured interaction described above is that of Bethe[6] and Peierls[7] which we formulate in Sec. II. A search for continuous second-order transitions to an ordered state which need not, however, be the state of lowest free energy, is carried out in Sec. III. The results of the approximation are presented in Sec. IV, and are discussed in Sec. V.

II. BETHE-PEIERLS APPROXIMATION

The Hamiltonian of the lattice gas model we consider is

$$H=\tfrac{1}{2}\sum_{i,j} v_{ij}n_i n_j\,, \qquad (2.1)$$

where the n_i's are either zero or one and v_{ij} is infinite if i is equal to j, equals v if i and j are nearest neighbors, equals $-\bar{v}$ if i and j are second nearest neighbors, and vanishes otherwise. The quantities v and $\bar{v}$ are positive. Because of the infinite repulsion between particles on the same site, the above model can be easily related to an Ising model of a spin system in an external field governed by the Hamiltonian

$$H=\tfrac{1}{4}\sum_{i\neq j} J_{ij}\sigma_i\sigma_j-\mathcal{H}_0\sum_i \sigma_i\,, \qquad (2.2)$$

where the σ_i's are either plus or minus one, J_{ij} is equal to J if i, j are nearest neighbors, is equal to $-K$ if i, j are second nearest neighbors, and vanishes otherwise. The quantities in the two Hamiltonians are related by the equations

$$\sigma_i=1-2n_i\,,\quad v=2J,\quad \bar{v}=2K. \qquad (2.3)$$

In addition the external field of the magnetic system is related to the chemical potential μ of the lattice gas according to

$$\mathcal{H}_0=\tfrac{1}{4}(v\gamma-\bar{v}\bar{\gamma}-2\mu)\,, \qquad (2.4)$$

where γ and $\bar{\gamma}$ are the number of nearest- and second-nearest-neighbor pairs and are equal to six in the triangular lattice. The magnetic free energy per spin is related to the pressure of the lattice gas according to

$$-f_{\mathrm{MAG}}=pa-\tfrac{1}{8}[4\mu-(v\gamma-\bar{v}\bar{\gamma})]\,, \qquad (2.5)$$

with a the area of the cell absorption site. We find it convenient to perform the calculations using the magnetic description but will present our results in the language of the lattice gas.

The order parameter of the antiferromagnet is related to the difference in sublattice magnetizations and is uniquely defined only when a choice has been made as to the number of sublattices into which the system will be divided. We choose a division into three sublattices as shown in Fig. 1. With this choice there are three order parameters of which two are linearly independent. The three order parameters may be taken to be

$$\xi_1 = \tfrac{1}{2}[\langle\sigma_2\rangle - \langle\sigma_3\rangle], \qquad \xi_2 = \tfrac{1}{2}[\langle\sigma_3\rangle - \langle\sigma_1\rangle],$$

$$\xi_3 = \tfrac{1}{2}[\langle\sigma_1\rangle - \langle\sigma_2\rangle],$$

where the brackets indicate ensemble averages and the subscripts now refer to the particular sublattice. There are also three distinct phases possible, a disordered and two ordered phases. In the first state all three order parameters vanish, in the second state one vanishes and the other two are of equal nonzero magnitude and opposite sign, while in the third state all are distinct and nonzero.

The Bethe-Peierls approximation may be formulated in one of two ways. The first and probably most familiar method is to view the approximation as an extension of simple mean-field theory. We consider a cluster of particles and take account of the interaction of the central spin with its nearest and second nearest neighbors exactly, but treat the interaction of the other spins in the cluster with each other and with other spins in the system by a mean field. Thus, considering a cluster with a spin on the ith sublattice at the center (i equals 1, 2, or 3), and labeling the lth spin on sublattice i $\sigma_i{}^l$, we may write the Hamiltonian of this cluster in the form

$$H_i = \sigma_i\left(\tfrac{1}{2}J\sum_{l=1}^{3}\sigma_j^l + \tfrac{1}{2}J\sum_{l=1}^{3}\sigma_k^l - \tfrac{1}{2}K\sum_{l=1}^{6}\sigma_i^l - \mathcal{H}_0\right) - \mathcal{H}_{ii}\sum_{l=1}^{6}\sigma_i^l - \mathcal{H}_{ij}\sum_{l=1}^{3}\sigma_j^l - \mathcal{H}_{ik}\sum_{l=1}^{3}\sigma_k^l, \quad (2.6)$$

where the $\mathcal{H}_{ij}$ are nine mean fields which must be determined self-consistently.

Defining

$$s = e^{\beta\mathcal{H}_0}, \qquad t = e^{\beta J/2}, \qquad u = e^{-\beta K/2}, \qquad x_{ij} = e^{\beta\mathcal{H}_{ij}},$$

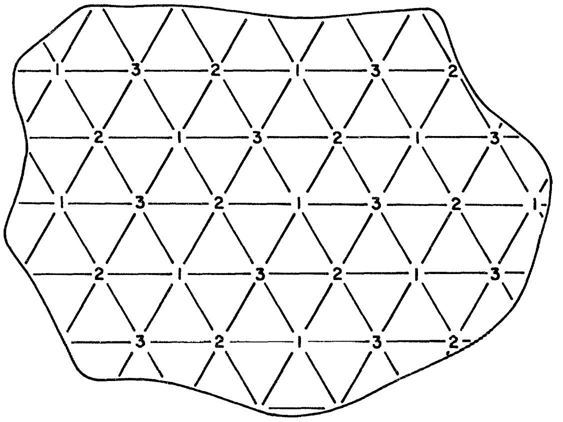

FIG. 1. Division of the triangular lattice into three sublattices.

and

$$S(x) = x + x^{-1}, \quad (2.7)$$

one obtains for the partition function of this cluster

$$Z_i = s\,S^6(x_{ii}u^{-1})\,S^3(x_{ij}t^{-1})\,S^3(x_{ik}t^{-1}) + s^{-1}S^6(x_{ii}u)\,S^3(x_{ij}t)\,S^3(x_{ik}t). \quad (2.8)$$

The ensemble average of the value of the spin at the center of the cluster is obtained from Z_i by means of

$$\langle\sigma_i\rangle = s\,\frac{\partial \ln Z_i}{\partial s}. \quad (2.9)$$

A useful relation between the external field, the average value of the central spin, and the unknown mean fields is obtained by performing the indicated differentiation in Eq. (2.9) and combining with Eq. 2.8). The result is

$$s^2 = \frac{(1+\langle\sigma_i\rangle)\,S^6(x_{ii}u)\,S^3(x_{ij}t)\,S^3(x_{ik}t)}{(1-\langle\sigma_i\rangle)\,S^6(x_{ii}u^{-1})\,S^3(x_{ij}t^{-1})\,S^3(x_{ik}t^{-1})}, \quad (2.10)$$

where $i = 1, 2, 3$ and $i \neq j \neq k$. The nine mean fields $\mathcal{H}_{ij}$, or equivalently, the nine quantities x_{ij} are ancillary unknowns and may be eliminated from the calculation by solving for them in terms of the unknown spin expectation values in the following way. From the form of the Hamiltonian of Eq. (2.6) it follows that

$$\langle\sigma_i\rangle = \tfrac{1}{6}\,x_{ii}\,\frac{\partial \ln Z_i}{\partial x_{ii}}. \quad (2.11)$$

The equation which results on differentiation may be solved for x_{ii} and yields

$$x_{ii}^2 = g(\langle\sigma_i\rangle, \langle\sigma_i\rangle, u), \quad (2.12)$$

$$g(a, b, v) \equiv \tfrac{1}{2}(1-b)^{-1}[(b-a)v^{-2} + (b+a)v^2 + r(a, b; v)], \quad (2.13)$$

$$r(a, b; v) = r(b, a; v) \equiv [(b-a)^2v^{-4} + (b+a)^2v^4 + 2(2-b^2-a^2)]^{1/2}. \quad (2.14)$$

Similarly,

$$\langle\sigma_j\rangle = \tfrac{1}{3}x_{ij}\,\frac{\partial \ln Z_i}{\partial x_{ij}}, \qquad i \neq j$$

which yields

$$x_{ij}{}^2 = g(\langle\sigma_i\rangle, \langle\sigma_j\rangle, t), \quad i \neq j. \quad (2.15)$$

The three unknown spin expectation values are now determined self-consistently by substituting the expressions for x_{ii} and x_{ij} into the three equations for s^2 given by Eq. (2.10). With the mean fields eliminated in this manner, the self-consistent equations for the spin expectation values can be written

$$s^2 = F(\langle\sigma_1\rangle; \langle\sigma_2\rangle, \langle\sigma_3\rangle) = F(\langle\sigma_2\rangle; \langle\sigma_3\rangle, \langle\sigma_1\rangle) = F(\langle\sigma_3\rangle; \langle\sigma_1\rangle, \langle\sigma_2\rangle), \quad (2.16)$$

where

$$F(a; b, c) = F(a; c, b)$$

$$= [\,(1+a)/(1-a)]\,H^2(a,a,u)\,H(a,b,t) \times H(a,c,t)\,, \quad (2.17)$$

and

$$H(a,b,v) = \{[g(a,b,v)\,v^2+1]/[g(a,b,v)+v^2]\}^3\,. \quad (2.18)$$

In general, these equations will have more than one solution for a given temperature and external field. Without an expression for the free energy, one can not determine which of the possible solutions will obtain. The nearest-neighbor correlation functions $\langle\sigma_i\sigma_j\rangle$ and the second nearest-neighbor correlation function $\langle\sigma_i\sigma_i\rangle$ may be determined by differentiating the cluster partition functions with respect to the appropriate parameters and eliminating the mean fields by means of Eqs. (2.12) and (2.15). The results are

$$\langle\sigma_i\sigma_j\rangle = (1-t^4)^{-1}[1+t^4-t^2 r(\langle\sigma_i\rangle\,,\,\langle\sigma_j\rangle\,;t)]\,, \quad i\neq j \quad (2.19)$$

$$\langle\sigma_i\sigma_i\rangle = (1-u^4)^{-1}[1+u^4-u^2 r(\langle\sigma_i\rangle,\langle\sigma_i\rangle;u)]\,, \quad (2.20)$$

where $r(a,b;v)$ is given in Eq. (2.14). In the limit of high temperatures, the above correlation functions approach the mean field result

$$\langle\sigma_i\sigma_j\rangle \rightarrow \langle\sigma_i\rangle\langle\sigma_j\rangle \qquad \text{all } i,j,$$

as T increases without limit. The low-temperature limit of the correlation functions differ reflecting the difference between the antiferromagnetic coupling of nearest-neighbor spins and the ferromagnetic coupling of second-neighbor spins. One finds

$$\langle\sigma_i\sigma_j\rangle \rightarrow |\,\langle\sigma_i\rangle+\langle\sigma_j\rangle\,| - 1 \qquad \text{for } i\neq j \text{ and } T\rightarrow 0\,, \quad (2.21)$$

$$\langle\sigma_i\sigma_i\rangle \rightarrow 1 \qquad \text{for } T\rightarrow 0\,. \quad (2.22)$$

The second formulation of the Bethe-Peierls approximation is a formulation in terms of the free-energy of the system. The magnetic energy per site, e, of the Ising model obtained from Eq. (2.2) can immediately be written in terms of the two-particle correlation functions and the spin expectation values in the form

$$e = \tfrac{1}{2}J\,(\langle\sigma_1\sigma_2\rangle+\langle\sigma_1\sigma_3\rangle+\langle\sigma_2\sigma_3\rangle) - \tfrac{1}{2}K\,(\langle\sigma_1\sigma_1\rangle+\langle\sigma_2\sigma_2\rangle+\langle\sigma_3\sigma_3\rangle) - \tfrac{1}{3}\mathcal{H}_0\,(\langle\sigma_1\rangle+\langle\sigma_2\rangle+\langle\sigma_3\rangle)\,. \quad (2.23)$$

The problem is to express the entropy or an approximation to it in these same terms. The Bethe-Peierls approximation to the entropy per site of the system is derived for an Ising ferromagnet in an interesting and lucid paper of Kikuchi.[3] The method is easily generalized to the interaction of interest to us. We define the following auxilliary variables:

$x(a) \equiv \tfrac{1}{2}(1-\langle a\rangle)$, $x_1 = x(\sigma_1)$, $x_2 = x(-\sigma_1)$, $x_3 = x(\sigma_2)$,
$x_4 = x(-\sigma_2)$, $x_5 = x(\sigma_3)$, $x_6 = x(-\sigma_3)$;
$y(a,b) \equiv \tfrac{1}{4}(1-\langle a\rangle-\langle b\rangle+\langle ab\rangle)$,
$y_1 = y(\sigma_1,\sigma_2)$, $y_2 = y(\sigma_1,\sigma_2)$, $y_3 = y(-\sigma_1,\sigma_2)$,
$y_4 = y(-\sigma_1,\sigma_2)$, $y_5 = y(\sigma_1,\sigma_3)$, $y_6 = y(\sigma_1,-\sigma_3)$,
$y_7 = y(-\sigma_1,\sigma_3)$, $y_8 = y(-\sigma_1,-\sigma_3)$, $y_9 = y(\sigma_2,\sigma_3)$,
$y_{10} = y(\sigma_2,-\sigma_3)$, $y_{11} = y(-\sigma_2,\sigma_3)$, $y_{12} = y(-\sigma_2,-\sigma_3)$;
$z_1 = y(\sigma_1,\sigma_1)$, $z_2 = z_3 = y(\sigma_1,-\sigma_1)$, $z_4 = y(-\sigma_1,-\sigma_1)$,
$z_5 = y(\sigma_2,\sigma_2)$, $z_6 = z_7 = y(\sigma_2,-\sigma_2)$, $z_8 = y(-\sigma_2,-\sigma_2)$,
$z_9 = y(\sigma_3,\sigma_3)$, $z_{10} = z_{11} = y(\sigma_3,-\sigma_3)$, $z_{12} = y(-\sigma_3,-\sigma_3)$.

The Bethe-Peierls approximation to the entropy per site is given by the expression

$$s = \tfrac{11}{3}\sum_{i=1}^{6} x_i \ln x_i - \sum_{i=1}^{12} y_i \ln y_i - \sum_{i=1}^{12} z_i \ln z_i\,. \quad (2.24)$$

The magnetic free energy per site is then constructed from Eqs. (2.23) and (2.24) and depends on twelve unknowns, the three $\langle\sigma_i\rangle$ and the nine $\langle\sigma_i\sigma_j\rangle$.

The equivalence of the two formulations is easily established. Upon setting to zero the variation of the free energy with respect to variations in any of the functions $\langle\sigma_i\sigma_j\rangle$, with i not equal to j, one obtains the expression for these six correlation functions given by Eq. (2.19). Similarly, setting the variation with respect to $\langle\sigma_i\sigma_i\rangle$ equal to zero yields the expressions for these three correlation functions given in Eq. (2.20). Lastly, setting the variation with respect to $\langle\sigma_i\rangle$ equal to zero yields the three self-consistency equations of Eq. (2.16) which determine the spin expectation values themselves. With the explicit expression for the free energy, the various solutions of the self-consistency equations can be checked to determine which solution is that of the lowest free energy.

III. POSSIBILITY OF SECOND-ORDER TRANSITIONS

In this section we wish to determine whether the self-consistency equations given in Eq. (2.16) permit transitions between an ordered and disordered state in which the order parameters characterizing the ordered solution go continuously to zero. To do this we write two of the consistency conditions in the form

$$F(\langle\sigma_1\rangle;\langle\sigma_2\rangle,\langle\sigma_3\rangle) - F(\langle\sigma_2\rangle;\langle\sigma_3\rangle,\langle\sigma_1\rangle) = 0\,, \quad (3.1)$$

$$F(\langle\sigma_2\rangle;\langle\sigma_3\rangle,\langle\sigma_1\rangle) - F(\langle\sigma_3\rangle;\langle\sigma_1\rangle,\langle\sigma_2\rangle) = 0. \quad (3.2)$$

The third consistency equation merely determines the average spin values in terms of the external field. The above equations are identically satisfied in the disordered phase in which $\langle\sigma_1\rangle = \langle\sigma_2\rangle = \langle\sigma_3\rangle = \sigma$, where σ is the average magnetization per site. We wish to determine whether there exists another solution to these equations in which each sublattice magnetization differs infinitesimally from its value in the disordered phase. As we are interested in phase transitions in the lattice gas at constant density, we shall investigate transitions in the Ising model at constant magnetization.

As

$$3\sigma = \langle\sigma_1\rangle + \langle\sigma_2\rangle + \langle\sigma_3\rangle ,$$

then

$$\delta\langle\sigma_3\rangle = -\,\delta\langle\sigma_1\rangle - \delta\langle\sigma_2\rangle .$$

Varying both Eqs. (3.1) and (3.2) with respect to $\langle\sigma_1\rangle$ and $\langle\sigma_2\rangle$ at constant σ yields the same condition:

$$\frac{\partial F(\langle\sigma_1\rangle;\langle\sigma_2\rangle,\langle\sigma_3\rangle)}{\partial\langle\sigma_1\rangle} = \frac{\partial F(\langle\sigma_1\rangle;\langle\sigma_2\rangle,\langle\sigma_3\rangle)}{\partial\langle\sigma_2\rangle} ,$$

with the derivatives evaluated at $\langle\sigma_1\rangle = \langle\sigma_2\rangle = \langle\sigma_3\rangle = \sigma$. With the use of Eq. (2.16) and Eq. (2.7), this may be expressed in the more transparent form

$$\frac{\partial \mathcal{H}_0(\langle\sigma_1\rangle,\langle\sigma_2\rangle,\langle\sigma_3\rangle)}{\partial\langle\sigma_1\rangle} = \frac{\partial \mathcal{H}_0(\langle\sigma_1\rangle,\langle\sigma_2\rangle,\langle\sigma_3\rangle)}{\partial\langle\sigma_2\rangle} , \qquad (3.3)$$

with the derivatives evaluated at $\langle\sigma_1\rangle = \langle\sigma_2\rangle = \langle\sigma_3\rangle = \sigma$. In terms of the lattice-gas variables, this condition is

$$\frac{\partial \mu(\langle n_1\rangle,\langle n_2\rangle,\langle n_3\rangle)}{\partial\langle n_1\rangle} = \frac{\partial \mu(\langle n_1\rangle,\langle n_2\rangle,\langle n_3\rangle)}{\partial\langle n_2\rangle} ,$$

with the derivatives evaluated at $\langle n_1\rangle = \langle n_2\rangle = \langle n_3\rangle = n$. Before solving Eq. (3.3), it is necessary to choose a ratio of the ferromagnetic to antiferromagnetic coupling strengths. From Eq. (2.3), it is seen that this ratio is also that of the strengths of the attractive and repulsive interactions in the lattice gas. A value of 0.2 for this ratio was chosen as it is appropriate to the interactions between helium atoms adsorbed on graphite. With this ratio, solution of Eq. (3.3) shows that the consistency conditions do admit second-order transitions from the disordered to an ordered phase. The locus of these transition temperatures in the temperature density plane is shown in Fig. 2. The temperature is measured in units of J and the density is only shown between zero and one-half as the diagram is symmetric about one-half.

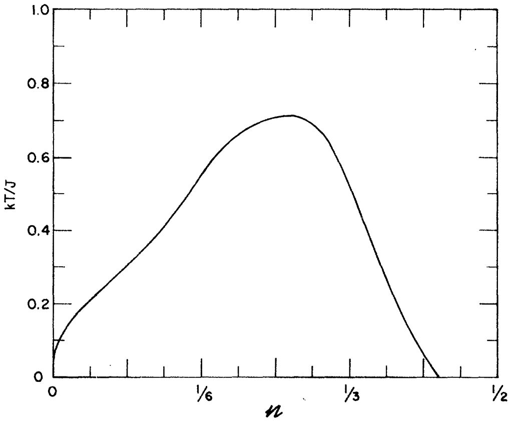

FIG. 2. Locus of possible continuous phase transitions in the temperature-density plane. Only one-half of the complete diagram, which is symmetric about density one-half, is shown.

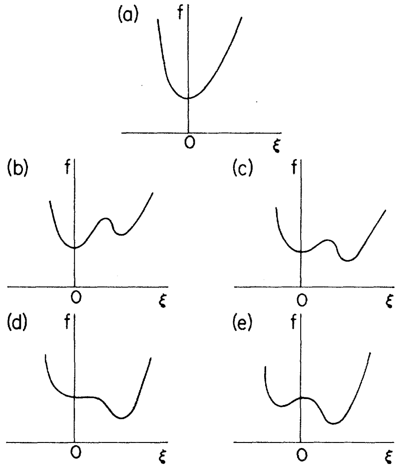

FIG. 3. The free energy per site vs order parameter is shown schematically at a fixed density at five progressively decreasing temperatures. The sequence is described in the text.

IV. RESULTS

To determine the phase diagram of the model in the Bethe-Peierls approximation, the average sublattice magnetizations were varied keeping the average total magnetization fixed, and the minimum of the free energy was sought. The results of this procedure are as follows.

There is no transition from the disordered phase to an ordered phase in which all order parameters are distinct and nonzero. There are transitions to the ordered phase characterized by one vanishing order parameter and two nonzero order parameters of equal magnitude $|\xi|$, and of opposite sign. As there can be no ambiguity, this phase shall be referred to henceforth as the ordered phase.

There are no second-order transitions between the ordered and disordered phase. All transitions are first order with the order parameter changing discontinuously across the phase boundary. It is of interest to explicate the reason why the continuous phase transitions which were found to be permitted in Sec. III are not obtained. This is most easily done with the aid of Fig. 3 which shows schematically a series of plots of the free energy per site,

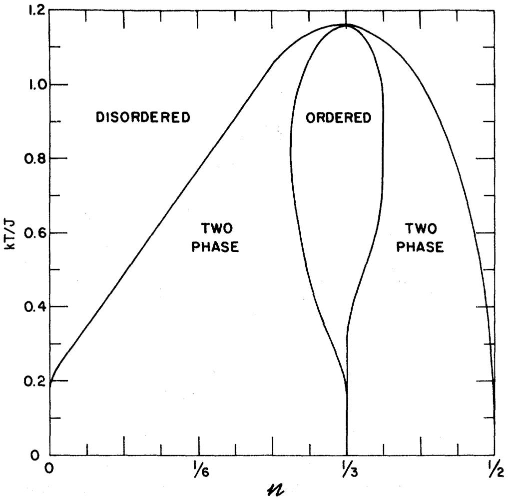

FIG. 4. Phase diagram obtained from the Bethe-Peierls approximation in the temperature-density plane. Only one-half of the complete diagram, which is symmetric about density one-half, is shown.

f, vs order parameter ξ. All plots are at the same magnetization but different temperatures.

The temperature in Fig. 3(a) is very high and the free energy has but one minimum at the disordered phase, ξ equals zero. As the temperature is lowered, the situation shown in Fig. 3(b) develops. There are now two minima, corresponding to the disordered phase, and to an ordered phase with a finite value of ξ. The system is still in the disordered phase as the free energy attains its lowest value there. Between Figs. 3(b) and 3(c) the system has undergone a first-order transition to the ordered phase. The extremum at $\xi = 0$ is still a minimum and at a nearby value of ξ the free energy has a local maximum. At the temperature at which a continuous transition is possible, these two nearby extrema merge as shown in Fig. 3(d). The system, of course, is in the ordered phase with a finite value of ξ. Lastly, if the temperature is lowered still further, both minima correspond to possible ordered states and the extrema at $\xi = 0$ is a maximum. In summary then, the first order transition takes place at a higher temperature than the continuous transition so that the latter is not seen.

The phase diagram in the temperature-density plane is shown in Fig. 4. As in Fig. 3 the temperature is measured in units of J and only one-half of the symmetrical phase diagram is plotted. Again the ratio of strength of the attractive to repulsive interaction is 0.2. The maximum transition temperature occurs at a density of one-third and has a value $kT/J = 1.165$. As at all other densities the transition is first order. At density one-third, the latent heat per particle is 0.788 in units of J.

Figure 5 shows the phase diagram as a function of chemical potential and temperature, both measured in units of J. In general, this diagram is symmetric about μ/J equal to $\gamma - \tilde{\gamma} K J^{-1}$. For the triangular lattice, the number of nearest-neighbor pairs, γ, and second-neighbor pairs, $\tilde{\gamma}$, is six. As we have chosen K/J to be 0.2, the diagram is symmetric about 4.8.

The behavior of the order parameter as a function of temperature at a density of one-third is shown in Fig. 6. As the temperature increases, the order parameter decreases from the value unity to 0.823 just below the transition temperature. Lastly, the specific heat per particle at constant area is plotted in Fig. 7 for a density of one-third. Its limiting values as the temperature approaches the transition temperature from below and above are 4.1 and 0.84, respectively, in units of the Boltzmann constant.

V. DISCUSSION

The phase diagram in the temperature-density plane displays several features that one would expect to appear in an exact solution. The maximum transition temperature occurs at a density of one-third because at this density the system can form a superlattice which is energetically favorable and which encompasses all particles, while at other densities there are too many or two few particles to do so. For similar reasons it is expected that in a two-phase region, the density of the ordered phase is always

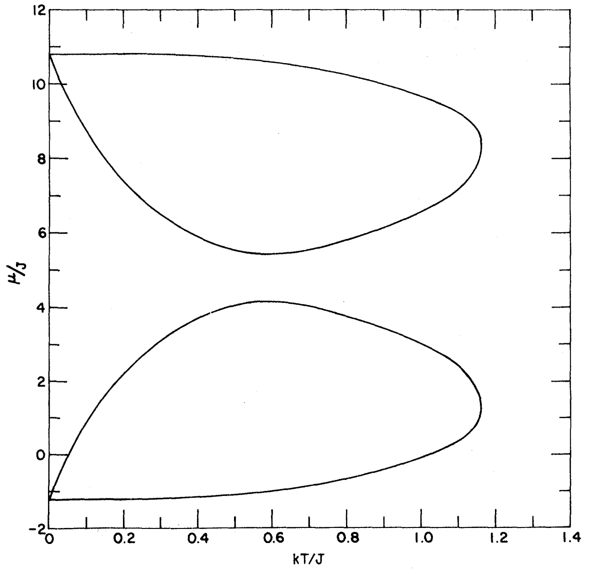

FIG. 5. Phase diagram obtained from the Bethe-Peierls approximation in the chemical potential-temperature plane. The diagram is symmetric about the value of μ/J equal to 4.8.

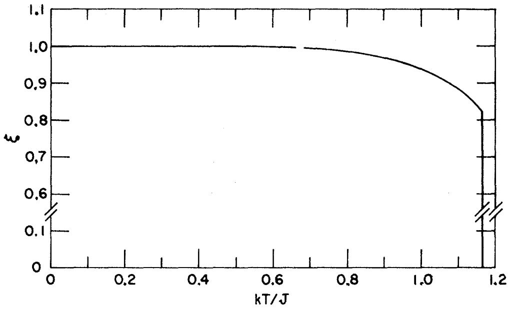

FIG. 6. Behavior of the order parameter with temperature at a density of one-third. The magnitude of the discontinuity in the order parameter of the transition temperature is 0.823.

close to one-third as is found. Further, due to the weak attractive interactions, the system, at arbitrarily low densities and temperatures, can cluster into an ordered phase in equilibrium with a low density phase which acts as its "vapor." The existence of a disordered phase in the vicinity of density one-half reflects the very large entropy of the disordered system at this density. In the purely repulsive system, a similar large value of the entropy prevents ordering at any temperature at this density.[1]

In addition to the above successes there are distinct faults in the results which are a consequence of the approximation used. Some of these faults will occur whenever the Bethe-Peierls approximation is employed while others are particular to the use of the approximation on a close packed lattice. As an example of a failure of the first kind, we note the existence of negative entropies. The expression for the entropy of Eq. (2.24) evaluated at density one-half and at vanishing temperature with the aid of Eqs. (2.21) and (2.22) yields the result $-5 \ln 2$. A similar result is obtained on the square lattice.[8] This result is due to the fact that the approximation assumes that all pairs are independent. This assumption has more serious consequences on a close-packed lattice. One such concerns the behavior of the correlation function $\langle n_i n_j \rangle$ for i not equal to j which can be related to $\langle \sigma_i \sigma_j \rangle$. It is found that as T approaches zero, $\langle n_i n_j \rangle$ in the state obtained approaches zero for all densities less than $\frac{1}{2}$. This result states that the nearest neighbor sites on an occupied site are always empty which is clearly not possible, for example, at densities greater than one-third. Another consequence is observed in the phase diagram in the chemical potential-temperature plane. Due to the attractive interaction it is certainly expected that at temperature equal to zero and at densities between one-third and two-thirds the system will consist of two phases in equilibrium of densities one-third and two-thirds. As the strength of this interaction is small but nonzero, it might be expected that this two phase equilibrium would persist at low temperatures.[9] This would imply in the μ-T diagram that the value of the chemical potential on the phase boundary would reach the value about which the diagram is symmetric (4.8 in Fig. 5) at a finite temperature but this is not observed. Again this is due to treating the pairs as independent and failing to include their correlations. These correlations are particularly important in bringing about a phase transition in the presence of repulsive interactions only. Their exclusion in the approximation is further demonstrated if the strength of the attractive interaction is set to zero in which case no phase transitions result: Rather, it is found that the consistency conditions admit ordered solutions, but the free energy of the disordered phase is always lower.

We conclude therefore that the low-temperature behavior as given in the approximation is not reliable at densities at which the correlation among pairs becomes important, i.e., densities greater than a value somewhat less than one-third. From the above argument concerning the behavior in the μ-T plane and the results displayed in Fig. 5, we can estimate a temperature on the order of $\frac{1}{2}J$ below which, at these densities, we expect qualitative differences between the exact and approximate results.

Another question of interest is whether neglect of the correlation between pairs on a close-packed lattice necessarily results in the absence of a second-order transition. On this point we can cite the work of Peierls[10] who considered order-disorder transitions in alloys of the kind AB_3 which have a close-packed fcc structure. In that calculation, all nearest-neighbor pairs in the cluster were treated equally so that correlations between pairs,

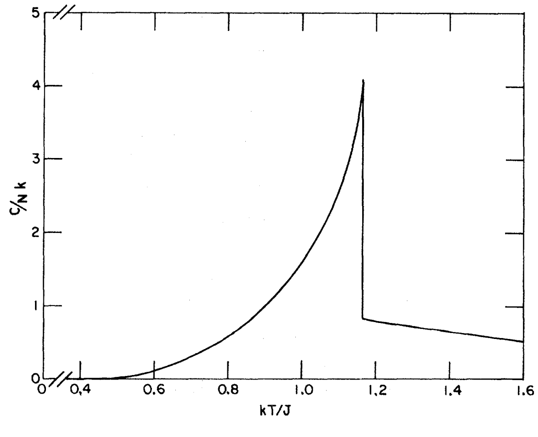

FIG. 7. Specific heat per particle at constant area vs temperature at a density of one-third.

although not treated exactly, were included in the approximation. A first-order transition resulted.

Experiments of He^4 [11] and He^3 [12] absorbed on graphite do show a large peak in the heat capacity at densities of one-third. The evidence appears to indicate that the transition is of second order. It must be noted, however, that irrespective of whether the model considered should evince a second-order transition, corrections to the exact results of the classical model due to the inherent quantum-mechanical nature of the helium system must be investigated.

ACKNOWLEDGMENTS

The authors wish to thank J. G. Dash for several useful conversations. They are particularly grateful to P. R. Zilsel for his insight and continued interest.

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*Research supported in part by the AEC and the NSF.

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PHYSICAL REVIEW A VOLUME 5, NUMBER 4 APRIL 1972

Theory of a Charged Boson Gas Using the Random-Phase Approximation*

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(Received 16 August 1971; revised manuscript received 5 November 1971)

The Brandow boson many-body theory is used to calculate the generalized dielectric constant within the random-phase approximation. The generalized dielectric constant obtained this way agrees with the Bogoliubov theory in the high-density limit and thus yields all of the well-known Bogoliubov results. The momentum distribution function for $\vec{k} \neq 0$ is also calculated. The treatment is fully number conserving.

I. INTRODUCTION

In a previous paper,[1] hereafter referred to as I, a study was made on a charged boson gas using the analogy to a fermion system with high spin degeneracy.[2] The noteworthy feature of the theory is that one introduces the concept of a hole in the boson system and thereby treats the dynamics of the condensate in a proper way. The number of particles is conserved without the aid of the chemical potential.[3] The well-known Brueckner-Goldstone cluster expansion is directly applied without any modification to the condensation operators. The result of I shows an exact agreement with the Bogoliubov theory of Foldy[4] both for the ground-state energy and the condensation fraction.

In this paper, this study is extended to the elementary excitation with the same Hamiltonian as used in I. In Sec. II the irreducible polarization part is calculated and then the generalized dielectric constant is obtained, which agrees again with the Bogoliubov theory in the high-density limit. This time-dependent dielectric constant yields all of the known results of Bogoliubov theory. In Sec. III we supplement I by calculating the momentum distribution function for $\vec{k} \neq 0$.

II. DIELECTRIC CONSTANT AND RELATED FUNCTIONS

The Hamiltonian is

$$H = \sum_{\vec{q}} \epsilon(q) a_{\vec{q}}^{\dagger} a_{\vec{q}} + \tfrac{1}{2} \sum_{\vec{q}}' v(q) [a_{\vec{q}}^{\dagger} a_0^{\dagger} a_{\vec{q}} a_0 + a_0^{\dagger} a_{\vec{q}}^{\dagger} a_0 a_{\vec{q}} + a_0^{\dagger} a_0^{\dagger} a_{\vec{q}} a_{-\vec{q}} + a_{-\vec{q}}^{\dagger} a_{\vec{q}}^{\dagger} a_0 a_0] , \quad (1)$$

with $\epsilon(q) = \hbar^2 q^2 / 2m$ and $v(q) = (4\pi e^2/\Omega)(1/q^2)$. Here Ω is the volume and N will represent the total number of particles. The prime indicates the absence